

FINAL REPORT

on

DEVELOPMENT OF A HIGHLY RELIABLE  
COMPOSITE BOARD FOR PRINTED CIRCUITRY  
FOR USE IN SPACE ENVIRONMENT

to

GEORGE C. MARSHALL  
SPACE FLIGHT CENTER  
NASA

October 30, 1970

by

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Contract No. NAS8-21424

Period Covered: June 28, 1968, through October 30, 1970

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November 19, 1970

National Aeronautics and  
Space Administration  
George C. Marshall Space  
Flight Center  
Huntsville, Alabama 35812

Attention Mr. W. P. Lewis

Gentlemen:

## Final Report on Contract NAS8-21424

Battelle is pleased to submit 11 copies of its Final Report on your program relating to the "Development of a Highly Reliable Composite Board for Printed Circuitry for Use in Space Environment".

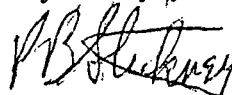
This report reviews the work done from the initiation of this project through October 30, 1970.

The new resin system P13N was selected as suitable for a high-temperature circuit board binder. When used in conjunction with an alumina filler and a tri-directional reinforcement, considerable improvements in the thermal conductivity and thermal expansion is obtained. A nickel-clad copper foil was shown to retain satisfactory adhesion after exposure to plating solutions. This, therefore, has been specified for this improved circuit board.

Materials and processes developed during the course of this program were utilized in the preparation of 100 square feet of circuit board for delivery to NASA.

We will appreciate any comments or suggestions you may have regarding this report. Editorial and art work changes were made to improve the quality of the rough draft approved. No changes, however, were made in either the basic information or the interpretation.

Very truly yours,



P. B. Stickney  
Project Coordinator

PBS:pls  
Enclosure (11)

cc: NASA  
George C. Marshall SFC  
Huntsville, Alabama 35812  
Attention R-P&VE Don Morris  
PR-SC, MS-1L, and MS-T

## FOREWORD

This report was prepared by Battelle Memorial Institute, Columbus Laboratories, under Contract NAS8-21424, "Development of a Highly Reliable Composite Board for Printed Circuitry for Use in Space Environment", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratories, George C. Marshall Space Flight Center, with Mr. W. J. Patterson serving as principal coordinator, and Mr. Don Morris serving as alternate coordinator.

### ABSTRACT

Materials, processes and fabrication techniques have been investigated for the development of a high-temperature circuit-board laminate.

High quality, void-free copper-clad laminates have been made using 7628/HS-1 style fiberglass reinforcements with filled polyimide matrices.

The fabricating characteristics of P13N resin appear suitable for use as a filled matrix in this circuit board development. High-fired, ball-milled alumina appears to be necessary to obtain the desired effects in the circuit board system.

Nickel-clad copper foil bonding surfaces appear to be another requirement for retention of good bond strengths after art work and plating sequences.

The fabrication cycle for this circuit board system is very dependent on the heating profile. Very rapid heating with quick loading is recommended. A stack approach to lamination was successfully used.

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## FINAL REPORT

on

### DEVELOPMENT OF A HIGHLY RELIABLE COMPOSITE BOARD FOR PRINTED CIRCUITRY FOR USE IN SPACE ENVIRONMENT

#### INTRODUCTION

This report describes the work done on the program from the initiation of the project, June 28, 1968, through September 30, 1970. Circuit boards for aerospace applications have several deficiencies which need to be overcome to provide more reliable and efficient service. Among the most critical deficiencies which may be mentioned is the thermal expansion in the three primary directions, with the greatest occurring in the thickness. Since this expansion is usually greater than that of the connectors joining the circuits on both sides of the circuit board, intolerable stresses are produced at the solder junctions. Moreover, the low-thermal conductivity of present circuit board laminates can result in localized heating with subsequent loss of circuit board strength.

This program, therefore, was directed towards resolving these deficiencies and developing a highly reliable and efficient circuit board. In pursuing this program, efforts were directed to the screening and evaluation of high-temperature resin systems; the use of reinforcements and fillers to provide the necessary controls on thermal expansion and conductivity without undue sacrifice of flexural strength; the development of fabricating and processing techniques, such as the use of a dissipation factor technique to assure optimum circuit board integrity; and finally, development studies directed toward improved resins for high-temperature service.

The information and techniques developed and acquired were utilized in the production of circuit boards for intensive evaluation and subsequent qualification testing.

#### OBJECTIVE

The objective of this program was the development of a circuit board with the following characteristics:

- (1) Shall have a linear coefficient of thermal expansion no greater than  $20 \times 10^{-6}$  ( $2.0 \times 10^{-5}$  in./in./C) along any of the three axes of the board when tested from -65 C to +200 C

- (2) Shall withstand thermal cycling between -65 C and +200 C without warping, degrading, or delaminating
- (3) Shall have a minimum thermal conductivity of  $15 \times 10^{-4}$  cal/sec/cm<sup>2</sup>/C/cm
- (4) Shall not support combustion in an oxygen atmosphere and be self-extinguishing when the source of flame is removed
- (5) Shall develop only minimal outgassing in the space environment
- (6) Shall be radiation resistant
- (7) Shall be machineable
- (8) Shall have sufficient strength at 200 C to support its own weight and that of the circuitry
- (9) Shall not become excessively brittle or susceptible to shock at -65 C
- (10) Shall be platable with copper, using standard methods
- (11) Shall provide adequate electrical properties
- (12) Shall be resistant to microbial attack and be sterilizable by thermal means.

The end product of this program should meet or exceed all of the requirements outlined in MSFC Specification 377A and be superior to G-10 epoxy-Fiberglas circuit boards.

## DISCUSSION

### Materials Review

An initial survey of the literature on circuit board materials, their processing, fabrication, and related problems was undertaken at the outset of the program. This survey was presented in the form of an Annotated Bibliography in the Annual Report. A low level of literature surveillance was continued during the additional period covered by this report and is reflected in the new materials studied and various references cited.



## Fabrics

Glass fabric Style 7628 presently used in many G-10 laminates is a plain weave consisting of a 42 x 32 (warp x fill) construction. Since the same yarn is used in both directions, the strength is slightly higher in the warp than in the fill direction, 225 and 200 pounds per inch, respectively. Although fiberglass yarns are presently available in several chemical compositions (E, Electrical; C, Chemical; S, High Strength), E grade is the lower cost general-purpose type and generally is used in G-10 laminates. Glass reinforcement construction, composition, and properties were discussed in detail in the First Quarterly Report and reviewed in the Annual Report.

The circuit board construction phase of this project was initiated with the use of a tridirectionally woven glass as a laminate core, faced with 7628 fabric for surface finish and control of flexural strength. An attempt was made to find a core material with balanced properties and in the course of this investigation, several fabrics were studied. The best combination available appears to be the Tricon reinforcement by Wimpfheimer. This has the following specification:

Fabric Spec	Wt, oz/sq yd	Lengthwise				Crosswise		Vertical	
		Ground		Stuffer		Fil.		Fil.	
		% Total	Dia., mils	% Total	Dia., mils	% Total	Dia., mils	% Total	Dia., mils
HS-1	15.0	50	0.25	5	0.25	24	0.25	21	0.21

The circuit board laminate as ultimately fabricated consists of five plies of glass fabric--a core of three plies of HS-1 fabric with a single ply of 7628 on either side. Attempts, however, were made to further simplify this structure by using heavier fabrics. Tricon fabric designated H-31, from Wimpfheimer Company, was evaluated for this use. This fabric has a weight of 2.6 lbs/sq yd with a thickness of 0.060 inch, all yarns untwisted. A total of four laminates were made with this form using the P13N matrix. Laminate I had an extremely low matrix content of 18.4 percent. Laminate II was intended to provide a higher matrix content, but only 24.9 percent was obtained. This is still well below the target value of approximately 40 percent. The flexural strengths of both laminates were below requirements. Consequently, Laminate III was fabricated using the same H-31 fabric, but with an additional layer of 7628 on each side. The resulting laminate showed no improvement in flexural strength.

Laminate IV was then fabricated using H-201 fabric from the same company. This material weighs 3.5 lbs/sq yd with a thickness of 0.079 inch. Single ply 7628 fabric was placed on both sides of the H-201. The resulting laminate also showed poor flexural strength especially in one direction. The results obtained on these laminates are summarized in Table 1, Appendix A.

Since the five-ply laminate (three plies of H-1, faced with 7628 fabric) does meet the flexural requirements, it was decided not to pursue further the effort to simplify the structure by use of a heavy fabric. Subsequent efforts emphasized fabrication and resin matrix studies.

### Fillers

An important approach to the control of the Z-direction thermal expansion and low thermal conductivity deficiencies of present circuit boards is the use of a filled matrix system. In pursuit of this target, a number of fillers were selected for screening in the normal G-10 resin system. In this manner, the resin compatibility, system handling characteristics, and ultimately the filler contribution to the expansion and conductivity properties of the circuit board laminates were determined. Since fillers nominally change the expansion and conductivity of resins as a function of the relative volumes used, they were evaluated at a 10 volume percent (V/O) level whenever possible. Exceptions were made for the very high surface area fillers which produce excessive thickening such that a 10 V/O loading cannot be used without adjustment of the solvent.

Comparative properties of a number of reinforcing and filling materials were discussed in the Annual Report. In general, most glasses and similar materials (quartz, silica, and some refractories) have thermal conductivities around  $1 \text{ to } 3 \times 10^{-3} \text{ cal/sec/cm}^2/\text{C/cm}$ . Asbestos and similar insulating materials have thermal conductivities about one-tenth ( $1 \text{ to } 3 \times 10^{-4} \text{ cal/sec/cm}^2/\text{C/cm}$ ) that of glass. Carbon, graphite, and some oxides and silicates have thermal conductivities from 10 to 100 times that of glass.

Most candidate reinforcing materials have thermal expansions around  $5 \times 10^{-6} \text{ in./in./C}$ . One refractory-type material, lithium aluminum silicate, is reported to have a significantly lower expansion, from  $-0.5 \text{ to } 0.3 \times 10^{-6} \text{ in./in./C}$ . This material, however, is presently available only as a powder.

The best resin compatibility and overall control of laminate properties was obtained with ball-milled A-14 high fired alumina. Although other grades of alumina might be used, it should be emphasized that a high fired grade is imperative. Failure to use such an alumina results in a porous, laminate with inferior electrical properties. This is very marked in laminates containing hydrated alumina filler which dehydrates at the laminating temperatures used for polyimides.

### Foils

"GT" treated copper foil is a new basic material which has had widespread acceptance for printed circuit boards in high-reliability applications. The properties of special interest are reported to be:

- (1) High-strength bonding to substrates. Bonding properties are reported to be at least ten times better than

untreated foils due to a special proprietary treatment of the foil surface which produces anchoring "teeth"

- (2) Superior corrosion, high-temperature and radiation resistance
- (3) Precision etchability resulting from uniform columnar grain structure and excellent weldability for high-strength circuit-board connections.

It was reported that the adhesion of copper to some high temperature laminates was destroyed by the gold plating step in circuit board utilization. It was postulated that the effect was due to solution of oxidized copper between the foil and the board. Accordingly, qualitative studies were made with several copper foils and plating solutions to verify this. One set of nickel-clad foil and G-2 coated foil were immersed in cyanide gold and acid gold solutions. Another set was heated to 600 F before immersion in the solutions. The G-2 coated foil which was heated to 600 F, was attacked immediately upon immersion in both the cyanide gold and acid gold solutions. The unheated G-2 coated foil survived for about 10 minutes in each solution before being attacked. The G-2 coating was completely stripped leaving the shiny copper foil substrate in all cases except one (Table 2, Appendix A), where it was obviously severely attacked but not completely removed. The nickel-clad foil both in the heated and unheated sets survived both solutions and appeared unaffected. The coatings were not attacked or removed and the copper substrates could not be seen. Thus it would appear that the nickel-clad copper should be more applicable for use in the circuit board since it offers much improved resistance to electroplating solutions. The results of the cyanide tests are summarized in Table 2.

One problem of concern regarding the new nickel-clad foil was its adhesion to the resin-glass substrate. One laminate containing a core of 3 layers of HS-1 fabric and a facing of 7628 on either side was made using Pl3N resin as the matrix. Nickel-clad copper foil was placed on one side with G-2 coated copper on the other. The material was processed according to standard procedure developed for this resin system. Adhesion tests show that the nickel clad foil had better adhesion to the substrate than the G-2 copper foil. Thus since the nickel clad foil showed both better resistance to cyanide and better adhesion than the G-2 foil, it was decided to use the nickel clad foil in the continuing developmental program. The results of comparative adhesion tests are shown in Table 3.

Although the nickel-clad foil does appear to circumvent the bonding surface oxidation encountered under polyimide laminating conditions, it does present some problems. Etching requires the use of either ferric chloride or ammonium persulfate etchant systems.

#### Resin Systems

Two distinctly different types of resin cure systems have been considered in this program. The first utilizing an addition type of cure,

crosslinks without the evolution of volatiles. The second or condensation type resins crosslink with evolution of generally volatile by-products. Hence, studies with this type of resin were directed toward improving their fabricability and reducing the evolution of volatiles associated with their use.

Addition-Cure Type Systems. Much of the background effort on fillers and reinforcements developed in this work has utilized a G-10 type binder as a point of reference. However, it was recognized that the G-10 epoxy resin system would not meet the rigorous heat resistance requirements. Accordingly, development emphasized work on more thermally stable binder systems. Various approaches to high temperature epoxy resin matrix systems are discussed in detail in the Annual Report.

Condensation-Cure Type Systems. Although this type of resin has good high temperature properties, high quality fabrications are difficult due to volatiles produced. Accordingly, fabricating studies were conducted using readily available polyimides, polyamide-imide and pyrrone resin binders. Most of the laminating studies were made using the procedure recommended by the resin suppliers. These consist of drying the impregnated cloth and conducting a partial cure to obtain a prepreg. This is then laid up and placed in a heated press. Lamination reportedly requires a rather rigidly controlled time-temperature program with contact pressure to advance the cure. This is followed by a time-temperature program with light pressure alternated with pressure release to vent volatile reaction products. Finally, full pressure is applied and the laminate is generally allowed to cure for several hours at temperature. Optimum laminate properties are attained by a postcure program at elevated temperatures. If adequate degassing is not attained, the laminate will have a significant void population and may even delaminate during the postcure program. Conversely, if pressure is applied too late, the binder will not flow and bond adequately between plies.

Most of the resin evaluation studies were discussed in the Annual Report. However, additional studies subsequent to the Annual Report resulted in the selection of a primary resin system and are discussed in detail in this report.

Pl3N Resin. This resin system was recently introduced by TRW. It is characterized by a fully imidized low-molecular-weight intermediate stage which melts and reacts at a higher temperature to form a high-molecular-weight polyimide by an addition type polymerization reaction. This type curing eliminates the principal disadvantage of conventional polyimides which cure by a condensation reaction with the evolution of volatile products and a resulting tendency to form porous laminates. The Pl3N system was used in fabricating laminates for comparison to the AI-10 (polyamide-imide) system. Both the nickel clad and G-2 coated foil were used in the comparison of the adhesion to copper. Peel strengths (lbs/in.) for the combinations of copper and resins were as follows:

		<u>AI-10</u>	<u>P13N</u>
Nickel Clad Foil	Top	1.3	9.7
	Bottom	1.6	11.1
G-2 Foil	Top	2.7	4.9
	Bottom	4.5	--

These results are the average of 5 samples each and indicate that the P13N resin system has better adhesion to both the G-2 and nickel clad foil than does the AI-10 resin system. Since the values were in the target area it was decided to develop this system further, rather than continue with the AI-10 which was the primary choice during the writing of the Annual Report.

The P13N processing and curing schedule used was based on the manufacturer's recommendation. The fabric is coated with the resin matrix system and dried for one-half hour during which time the imidization process presumably is completed. The coated fabrics are then stacked and heated to 600 F when the appropriate pressure is applied. In an effort to determine the optimum temperature at which the pressure should be applied, the dissipation factors of the matrix systems were measured as a function of temperature. The dissipation factor showed an increase with increasing temperature. At about 400 C, the reading was off scale on the equipment and remained so after nearly an hour at 400 C. As the temperature was decreased below 400 C, the dissipation factor began to decrease. The sample was then reheated and the factor again increased. This anomalous behavior implies that the material is not really thermosetting but acts more like a thermoplastic resin at the higher temperatures. This probably reflects a somewhat lower glass transition temperature than the conventional polyimide resins have. (Figures 1 and 2, Appendix B)

This may leave something to be desired by way of a higher temperature (300-400 C) resin. The manufacturers' data on this material does indicate that a fiberglass laminate of P13N resin has a flexural strength of over 60,000 psi after exposure to 550 F (228 C) for 500 hours. Tests were reportedly conducted at the aging temperature. Accordingly, it is recognized that while the behavior may be somewhat thermoplastic at the higher temperatures (400 C), it should be satisfactory for applications requiring stability at 200 C.

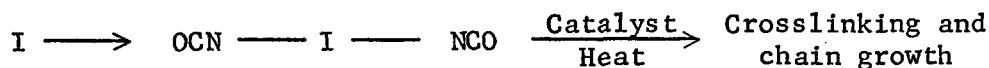
Other resins were screened, but these generally were more difficult to fabricate and had properties inferior to the P13N composites.

It was reported that the DuPont pyralin prepreg, 35-820 (polyimide based) showed very good adhesion to the nickel-clad copper facing. Accordingly a sample of this prepreg was obtained and used to replace the 7628 surface layer in the fabrication. The resulting laminate showed very poor adhesion between the copper and the prepreg. A sample of the DuPont polyimide resin 5077, reportedly used in the preparation of the 35-820 prepreg, was also used instead of P13N to impregnate the 7628 glass fabric. This laminate also showed poor adhesion between the copper and the 5077 prepreg.

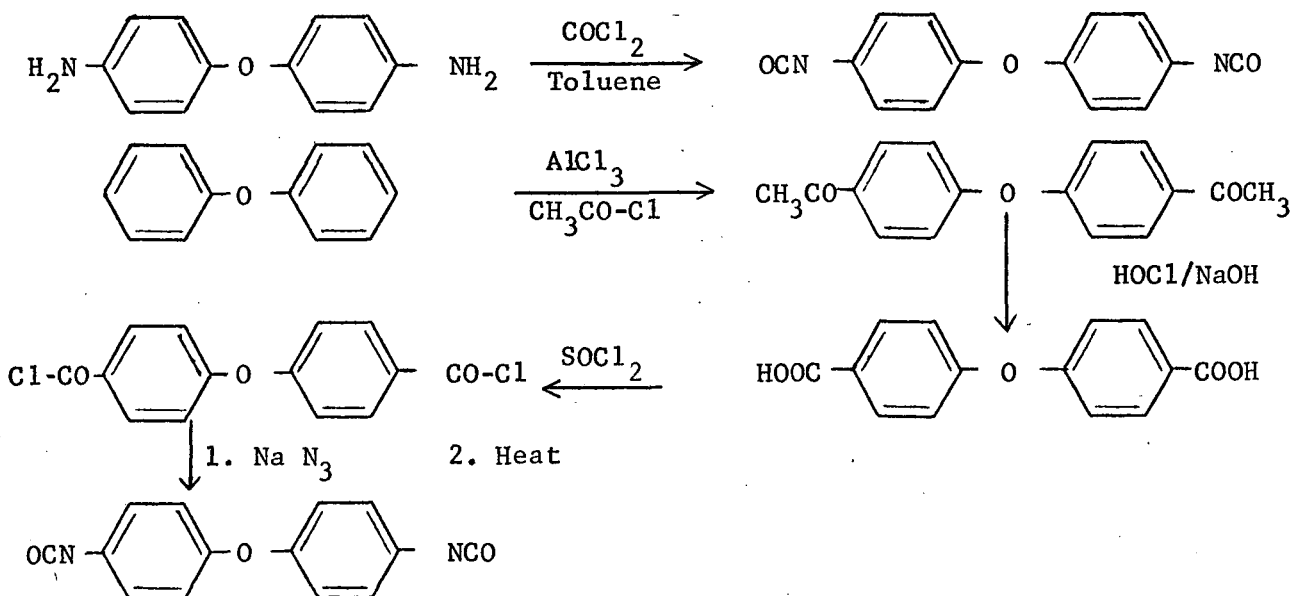
Other resin systems evaluated were XPI-182, a polyimide from American Cyanamide and a Stable Aromatic Polyester (SAP) from Carborundum. The XPI-182, like the 5077, showed poor adhesion to the copper. Efforts to prepare either a satisfactory SAP solution or dispersion for use in laminate fabrication have been unsuccessful. The SAP resin settled out in organic solvents and in aqueous dispersions. Subsequent literature on the SAP resin revealed that the material submitted could be fabricated only by sintering techniques such as are used in powder metallurgy. Accordingly, the flow and wettability of the grade studied eliminated it from further consideration as a circuit board binder.

### New Resin Development

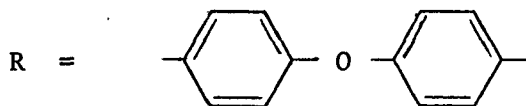
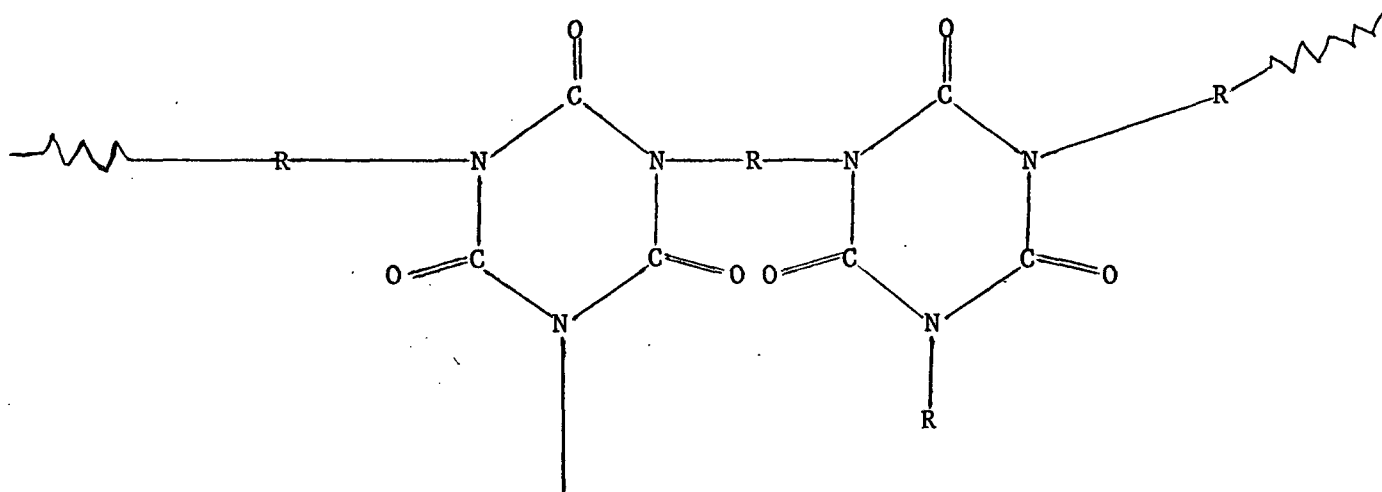
New-generation resins currently used as binders for high-temperature composites have two inherent problems: (1) evolution of volatiles during cure, and (2) generally poor processing characteristics. In order to overcome these difficulties, attempts were made to design a resin system based on the following chemistry where polymerization and crosslinking occur simultaneously without loss of volatiles:



For I, the first choices were diphenylether and 4,4'-diaminodiphenylether, the latter compound being commercially available from the Sumitomo Chemical Company, Osaka, Japan. The following conversions were carried out in high yields:



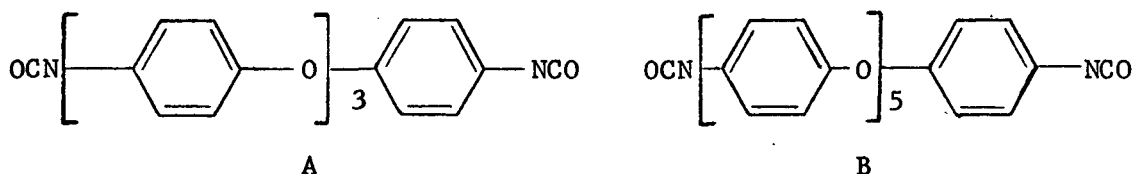
Polymerizations of these diisocyanates in the presence of phenylisocyanate using a double catalyst system composed of hexamethylenediamine and styrene oxide were carried out. The products of the polymerizations were polyisocyanurates having the following general structure:



The addition of phenylisocyanate helps decrease the degree of crosslinking during the polymerization by allowing longer linear chain sequences to develop.

On the basis of preliminary evaluations of test laminates prepared using the above-described poly(arylisocyanurate) binders, it appeared that a suitably tailored and developed poly(arylisocyanurate) might meet most of the requirements sought in improved, heat-resistant laminating resins. The experimental laminates demonstrated good thermal and mechanical properties. Cures of the resins were accomplished with significantly lower volatile losses than are experienced with resins that crosslink by condensation-type mechanisms. However, it was apparent that means for regulating the very rapid cure rates of the poly(arylisocyanurate) materials and moderating the high degrees of crosslinking obtained would have to be developed before the resins could find practical application as laminate binders. The most practical approach to this problem was felt to be through the use of higher molecular weight poly(phenylene oxide) precursors for the diisocyanate preparations. The

resulting diisocyanates would have lower functionalities than one isocyanate group per phenyl ring and, consequently, should polymerize to form less highly crosslinked structures and undergo cures more controllably than the lower molecular weight diisocyanates studied earlier. Accordingly, attempts were made to synthesize the two following diisocyanates A and B. Details on the synthesis procedure are given in Appendix A.



Progress was made in the synthesis of isocyanate moieties and reduction of the rate of final polymerization. An adequate moderating of cure rate was not achieved which would permit reduction to fabrication.

### Fabrication Studies

Efforts in this area were directed primarily towards a survey of laminate fabrication variables and the effect on the properties of the circuit board. These studies included (1) filler concentration, (2) prepreg drying, (3) laminating pressure, (4) laminate construction, (5) cure schedule and (6) stack laminating. Details relating to these studies are discussed in the corresponding titled sections which follow.

#### Filler Concentration

It was indicated earlier that two of the most critical requirements of the circuit board are the coefficient of thermal expansion and the thermal conductivity. A number of methods were originally considered to meet these requirements including the use of a truly three-dimensional fabric, which would minimize the expansion in the thickness direction of the board. However, the production and availability of this type of fabric was rather limited and costly, hence the use of an appropriate filler was investigated.

The A-14 hard-fired alumina filler in the resin formed a matrix which appeared to meet these requirements. A number of experimental laminates were fabricated in which the concentration of A-14 was varied to control the thermal expansion and thermal conductivity. The results are summarized in Table 4. Since the target values are  $20.0 \times 10^{-6}$  in./in./C and  $15.0 \times 10^{-4}$  cal/sec/cm<sup>2</sup>C/cm for the coefficient of thermal expansion and conductivity, respectively, a laminate fabricated from a matrix system containing 22.5 volume percent of the A-14 alumina system appears to meet these requirements. It should also be apparent from the results in Table 4 that a slight variation from this filler concentration (22.5 percent) would probably not be very critical and the laminate should still be within range of target values. Moreover, the matrix system with this concentration of A-14 filler appears to be very stable without the problem of settling out and sedimentation.



### Prepreg Drying

The procedure developed for the handling of the prepreg consists of drying in an oven for one-half hour at 150 F and then "B-staging" for an additional hour at 400 F. At the end of this period, the prepreps are fairly stiff and rigid and at subsequent fabrication there seems to be very little resin flow. It was felt that perhaps the "B-stage" had progressed too far. The prepreps were subsequently dried at 400 F for periods of 15, 30, and 45 minutes prior to laminate fabrication. The resulting laminates showed some degree of blistering indicating that there still seems to be some residual solvents or volatile matter which should be removed before fabrication.

### Laminating Pressure

The pressure generally used in the production of G-10 type circuit board is usually from 1000 to 1500 psi. In our efforts with the P13N resin, 1500 psi was normally used. Since this is a rather high pressure, it was decided to investigate the properties of the laminate using considerably less pressure. Accordingly, a series of laminates were fabricated at pressures of 100, 250, 500, and 1000 psi and the results compared with these fabricated at 1500 psi. Laminate characterization values are listed in Table 5.

The general appearance of the laminates made at the lower pressures were poor compared with these at higher pressures. Resin-rich and resin-poor areas were prevalent, due most likely to poor resin flow. The lower pressure laminates were also thicker and more uneven. Surprisingly, however, the mechanical properties were generally comparable to these of the higher pressure laminates. These results suggest that the laminates with the P13N resin system can be fabricated at lower pressures without any apparent significant loss of mechanical properties. This would further indicate that the pressure requirements are not critical, thus permitting a wider range and tolerance in the fabrication and manufacturing processes. From visual inspection and appearances, however, the laminates prepared under pressures of 1000 and 1500 psi seem to be the best.

### Laminate Construction

During the period covered by this report, a large number of experimental laminates were fabricated to improve the physical and electrical properties as well as processing techniques. The A-14 filler concentrations were varied to control thermal expansion and thermal conductivity. The results tend to show the inevitable trade-off characteristic of polymeric materials, i.e., a gain in one property results at the expense of another, in this instance lowering of peel strengths.

A special laminate was fabricated in which the copper facing sheets were coated with P13N, the 7628 fabric with a mixture of 50-50 P13N/AI-10, and the core of 3HS-1 fabric with AI-10 resin system. The P13N was applied to the copper layers because of better adhesion properties. The AI-10 system was used in the core for control of thermal expansion since the P13N resin

showed thermoplastic tendencies and it was felt that the thermal expansion might be relatively high. However, thermal expansion results have since indicated that the P13N system to be within target values and work on the use of P13N/AI-10 blends was discontinued. A general summary of these laminates is reported in Table 6. From these results it would appear that the target values listed are within range.

### Cure Schedule

The resin supplier's recommendation calls for heating in a 600 F press with a short contact heating time (30 seconds) before applying laminating pressure. In general this procedure was used in the fabrication of small size experimental circuit boards. In this situation the thermal capacity of the laminate does not greatly affect the equilibrium temperature of the press. However, when larger-sized circuit boards or a stack of circuit boards are placed in a preheated press, the thermal capacity is sufficient to reduce the press temperature. Accordingly, studies were conducted to determine whether modified cure programs should be used to fabricate circuit boards. It was found that different time-temperature heating profiles could be used to produce satisfactory laminates. Maximum temperatures and the loading time were found to be critical, however.

Most of the cure schedule work relates to stack laminating studies and additional details are presented under this heading. In general, a very rapid temperature rise permits only a short heating period prior to loading. If the time becomes too long or the temperature too high, gelation occurs and prevents flow. Conversely, premature loading after insufficient heating or at a too low temperature results in blister formation. Figure 3 correlates the time-temperature profile and loading for several laminates with the general laminate quality. Temperature profiles were determined by recording a corner temperature of the laminate with a fine gage thermocouple wire. The results demonstrate the critical nature of the process control.

### Stack Laminating

A preliminary attempt to stack and laminate this system similar to commercial practice appeared satisfactory. A stack consisting of three 3 x 3-inch circuit-board laminates separated by polished stainless steel sheets was laminated in a 650 F press. A slightly different processing cycle was used in this fabrication to determine whether an equilibrium thermal soak period would reduce internal stress and improve the circuit-board properties. This fabrication cycle consisted of laminating the stack under 1500 psi when the temperature reached 600 F in the center laminate. The system was held 15 minutes under equilibrium conditions and the temperature control cut back to 400 F. After the stack cooled under load to 400 F (about 1 hour), the entire stack was held for 1 hour at 400 F and 1500 psi.

Results of tests run on these laminates are as follows:

<u>Laminate Number</u>	<u>Thickness</u>	<u>Matrix</u>	<u>Flex kpsi</u>	<u>Peel lbs/in.</u>	
				<u>Top</u>	<u>Bottom</u>
36 A	.056	36.4	45	8.6	8.5
36 B	.058	39.6	46	7.2	7.2
36 C	.056	37.0	48	7.1	7.6

These results are generally comparable to those obtained from laminates which were individually prepared.

Another processing modification was explored to evaluate the criticality of the lamination procedure. This involved carrying the laminate stack to a higher temperature, 625 F, before applying the load. If feasible, this would provide an improved margin for assurance of complete volatile removal. These laminates did not flow and bond satisfactorily, indicating that preheating at temperatures too close to the preferred laminating condition will destroy fabricability.

Subsequent work with larger sized circuit boards, both individual and stacked lamination, confirmed the need to adjust the fabrication control to the temperature profile. This concept was discussed in an earlier section but dealt only with the fabricating single laminates. The cooling of the press platens is considerably greater for a stack of circuit board laminates than for a single circuit board. This, of course, is due both to the weight of materials in the laminates and to the weight of the separator sheets.

Initially, an attempt was made to compensate for the thermal capacity of the laminating charge by over heating the platens. This resulted in a time-temperature curve which more closely followed the fabrication curve for experimental sized boards. It was found, however, that exceedingly high initial platen temperatures would be required to effect the rate of heating used in the small samples. Further, the high initial platen temperatures resulted in a greater temperature spread across the area of the cauls. This was undesirable in view of the sensitivity of the gelation rate to temperature. A survey was made of the upper and lower caul temperatures at the center and four corners. It was found that temperature variations ran as high as 60 F for a common control setting. Caul temperature uniformity was markedly improved by insulation on all four sides of the platens and by installation of a thin sheet of asbestos (1/32 inch) between the caul plate and the platen. This, of course, reduced the rate of temperature rise in the laminate, but it eliminated hot spots in the cauls. A survey of caul temperatures after these changes showed a nearly constant temperature throughout the laminating area. The maximum temperature difference detected was about 10 F at 600 F and it was suspected that this was due to heat loss at the edges of the cauls.

Time-temperature profiles similar to the cure schedule studies were run for single and multiple laminates. It was found that the heating rate of the multiple lamination in the partially insulated press was sufficiently slower such that a longer contact time was required (Figure 4). In an effort to maintain a relatively rapid heating rate, preheating to a higher initial caul temperature (650 F) was continued. The press control temperature, however, was cut back to 610 F prior to insertion of the stack in the press. This resulted in equilibration of the laminate at about 600 F.

### Laminate Evaluation

In addition to the mechanical testing used routinely to evaluate laminate properties, several more specific tests were run. Mechanical property procedures and data were discussed in the Annual Report and in earlier sections of this report. Test procedures relevant to this section include (1) elevated temperature tests, (2) thermal cycling, (3) outgassing studies, (4) and copper adhesion.

### Elevated-Temperature Tests

Elevated-temperature tests specified for the G-10 circuit boards were run on laminates containing 22.5 and 25 percent A-14 filler with P13N resin. Samples were exposed to 300 F for 1 hour and then flex and peel strengths run at the test temperature. Property values for these laminates at the test temperatures were:

<u>Properties</u>	<u>Laminate 25% A-14</u>		<u>Laminate 22.5% A-14</u>	
	<u>R.T.</u>	<u>300 F</u>	<u>R.T.</u>	<u>300 F</u>
Flex, ksi Long.	42.0	31.0	42.0	35.0
Trans.	37.0	28.0	37.0	31.0
Peel (lbs/inch) Top	7.5	--	6.9	3.3
Bottom	7.0	--	7.3	--

These results show retention of about 75 percent in flex strength and about 50 percent in peel strength.

### Thermal Cycling Tests

Cycling tests programmed to thermally shock circuit board samples from -65 C to +200 C within 1 hour have been conducted for 14 days. The results are shown in Table 7 for flex and Table 8 for peel strength at the end of 14 days. Visual inspection and examination of the samples show discoloration of the copper but no evidence of delamination or warping. The test results show little loss in flex strengths, while there were about 80 percent or better retention of peel strengths.

### Outgassing Studies

A sample of Laminate 27620-15 was stripped of the copper facing on both sides and the weight loss on the substrate determined by TGA. The results are shown in Table 9. The initial weight loss was 0.57 percent per  $\text{cm}^2$  per hour from room temperature to 200 C. This exceeds the requirement of 0.2 percent/ $\text{cm}^2$ /hour. However, the steady state weight loss at 200 C for an extended period of time was essentially zero. Thus, the total weight loss would be very near the target requirements.

### Copper Adhesion to Substrate

Samples were prepared and submitted to NASA for evaluation. Initial feedback of results indicated some problem in drill-through adhesion of the copper to the substrate. All other tests conducted were reported to be satisfactory. Efforts were made to improve the drill-through adhesion of the copper to the board by upgrading adhesion. This problem does not seem to occur with the G-10 boards containing epoxy resin binders. Since the objective of the current program is to produce a board equal to or better than the G-10, this in effect poses a problem since epoxy resins are universally recognized as having better bonding properties than most resin systems--certainly than the polyimides. Moreover, the problem is accentuated by the relatively small surface area of the copper remaining--about 1/16 of an inch in diameter through which a hole about 1/32 inch is drilled. There is thus very little area for the copper to adhere to. The substrate fiber-glass resin is relatively soft compared to the nickel-coated copper. Hence, in drilling through this material, one is suddenly confronted with a relatively harder material with the resulting tendency to create an impact on the copper--enough to physically push it off rather than drilling through it. This would be particularly so if the point of the drill were somewhat dull. It should be emphasized that the alumina filler used in this system is an abrasive. It is quite likely, therefore, that these circuit boards will quickly dull a conventional drill. The use of a carbide-tipped drill, therefore, might be helpful in reducing this problem. Other drilling procedures such as laser or ultrasonic also might be helpful.

It should be noted that copper adhesion of earlier samples was measured at around 7 to 8 lbs/inch of peel. Somewhat better peel strength (possibly approaching 10 lbs/inch) appears to be characteristic of the production foil. However, in view of the overall properties of the circuit board this may not eliminate the problem.

### Quality Control in Prototype Lamination

Although visual inspection is adequate to establish gross quality of the experimental circuit boards, it was considered advisable to establish additional criteria for prototype production. Accordingly, temperature profiles of the laminate stack and each of the caul plates were monitored during the laminating cycle. This provided a running record of the heater control and press operation. Any deviation from the normal pattern would make the quality of the laminate set suspect.

Laminates which looked satisfactory were randomly checked for factors such as peel and porosity. These spot checks were made on the strips trimmed from the edges of the laminates. Although these peel and porosity tests are not rigorous procedures, the results indicate good quality laminates. Peel strengths were estimated by measuring the stripping load (around 35 ounces) with a spring scale and the specimen width (around 0.25 inch) with a steel rule. Estimated peel strengths for two sets of laminates ranged as shown in Table 10.

Although the procedure used in estimating these peel strengths admittedly is crude, it is believed that the peel strength of the prototype laminates are about 10 pounds per inch. Optical examination of these trim strips indicated the absence of voids.

Characterization of the chemically polished surface of a representative 12 x 12 inch circuit board was run on a Talysurf Profilometer\*. The results showed a center line average of 20 microinches across the board and 17 microinches with the board, both of which meet the G-10 specification. These values represent the cloth marking characteristics of the system without any improvement in surface by finishing.

The final qualification is based upon the projected weight-thickness relationship for a 12 x 12 inch circuit board, Figure 6. If reasonable precision is used in cutting to size, this correlation will indicate major variability in laminate construction. Areas of variability may include the thickness of P13N coating on the copper. Random checks of thickness indicated a variation of 2.0 to 2.4 mils. This represents a weight difference of about 1.5 grams per copper face. A second area of variability could be in the impregnation of the fabric. This also would affect the total board weight. Theoretical thickness projection is based upon previously used density values for the laminate components. Projection of the resin thickness assumes an average value of 2.2 mils for each face. Projection of the matrix assumes the system is 22.5 volume percent A-14 filler. Circuit boards checked against this correlation generally appear to have about 35 percent matrix and fall on or to the left of the zero void line. The 1 percent void line is based upon the substrate volume only.

#### Materials Evaluation for Production Run

Fifteen gallons of the P13N resin from TRW were received and trial laminates fabricated according to the standard procedure developed for this system. The peel strengths were lower than those previously obtained averaging about 6.2 lbs/in. In view of the difficulty encountered in drill-through adhesion with laminates having 8+ lbs/in. peel strength, these results indicated the problem. The failure in the peel tests was at the interface between the

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\* Engis Equipment Company, Morton Grove, Illinois.

resin and the treated surface of the copper foil. This failure could be due to the new batch of resin or the aging of the treatment on the foil surface. New copper foil was obtained and additional laminates fabricated using the new batch of resin. Two sets of laminates were fabricated--one using the alumina-filled resin brushed on the copper foil surface and another in which the unfilled resin was used. Results of the adhesion peel tests show slightly higher results, 8.6 lbs/in., 7.6 lbs/in., for the systems where the filled and unfilled resins were used. Since both of these results tend to be higher than those using the old copper foil, it appeared that part of the problem of poor adhesion was due to aging or contamination of the foil surface.

Accordingly, the foil surface, both old and new, was washed in a solution of 75 g/l of NaCN, rinsed and dried before laminates were fabricated. Laminates using the old foil showed peel strengths of 5.0 lbs/in. with failure observed between the matrix and the treated (nickel clad) foil surface. Laminates using the new foil showed relatively little peel strength with failure occurring between the nickel clad surface and the copper foil itself. Obviously, the adhesion of the nickel-clad treatment to the copper-foil surface in the new foil was not cyanide resistant so that the foil could not be used. Accordingly, this roll was returned to the supplier. The replacement roll showed satisfactory results after the same cyanide treatment.

It appears that quality control of the materials to be used is of prime importance, particularly in the translation from laboratory to production or large scale use. Precaution must be taken to insure that the materials obtained in bulk are of the same quality as smaller quantity samples used in development. For optimum results in the production of the circuit boards, the materials used in the fabrication should be characterized and property tolerances specified.

#### CONCLUSIONS

- (1) An improved circuit board system has been developed which meets most of the service requirements.
- (2) The combination of 7628 and HS-1 fabric seems adequate to meet the strength requirement of the laminate.
- (3) The 7628/HS-1 combination used in the sequence recommended is effective in giving a better balance of physical properties.
- (4) The use of HS-1 reinforcement is effective in reducing the thermal expansion normal to the laminate.
- (5) A-14 alumina is an effective filler for controlling thermal conductivity and expansion of this circuit board.
- (6) GT treatment of copper foil is effective in obtaining good bonding with polyimide systems.

- (7) Circuit boards produced with GT treated copper foil have been resistant to cyanide-containing baths.
- (8) Pl3N polyimide resin appears to have good potential for fabrication of quality products and the desired service life.

#### FUTURE WORK

- (1) Pl3N resin characterization studies should be conducted to establish meaningful materials specifications.
- (2) GT foil characterization studies should be made to determine allowable bonding surface variations.
- (3) Filler size and coupling agent correlations should be investigated to optimize circuit board properties and quality.



## APPENDIX A

### TABLES

TABLE 1. PROPERTIES OF LAMINATES WITH  
HEAVY FABRIC REINFORCEMENTS

Laminate Number		I	II	III	IV
Core fabric/pplies		H-31/1	H-31/1	H-31/1	201/1
Outer layers		None	None	7628	7628
Percent matrix		18.4	24.9	45.0	39.1
Thickness		0.046	0.050	0.065	0.073
Flex	Transverse	29	24	29	29
(Ksi)	Longitudinal	50	45	39	40

TABLE 2. RESULTS OF CYANIDE TESTS

Copper Foil	Cyanide Gold <sup>(a)</sup>	Acid Gold <sup>(b)</sup>
G-2 (as received)	Stripped in 10 min	Attacked in 10 min
G-2 (heated to 600 F)	Stripped immediately	Stripped immediately
Nickel clad (as received)	Unaffected	Unaffected
Nickel clad (heated to 600 F)	Unaffected	Unaffected

(a) Cyanide Gold: 10 g/l of 67 percent gold cyanide  
90 g/l KCN, used at  $20\text{ C} \pm 5\text{ C}$ .

(b) Acid Gold Solution: Temprix H.D. Sel-rex used at  $150\text{ F} \pm 5\text{ F}$ .

TABLE 3. ADHESIVE STRENGTH OF P13N  
BONDED COPPER FOILS

Sample	Peel Test Results, lbs/in.	
	G-2 Copper	Nickel-Clad Copper
1	4.76	7.24
2	4.53	7.58
3	4.60	7.91
4	4.68	8.19
Average	4.64	7.73

TABLE 4. EFFECTS OF CONCENTRATION OF A-14 ALUMINA ON CB PROPERTIES

Filler in Matrix Volume Percent	35	25	22.5	20
Laminate thickness (inch)	0.061	0.070-0.072	0.064-0.068	0.057
Laminate matrix content, percent	45.4	43.5	38.0	36.3
Peel (lbs/inch) Top	7.6	7.5	6.9	10.7
Bottom	7.8	7.0	7.3	6.7
Flex (ksi) Long.	41.0	42.0	42.0	49.5
Trans.	37.0	36.0	35.0	45.0
Conductivity ( $\times 10^{-6}$ ) (1)	14.8	10.9	14.7	11.4
CT/E ( $\times 10^{-6}$ ) (2)	22.4	18.2	20.0	20.0

(1) Conductivity  $\text{cal/sec/cm}^2/\text{C/cm}$ .

(2) Coefficient of thermal expansion (in./in./C).

TABLE 5. EFFECT OF PRESSURE ON LAMINATES

Pressure		100 psi	250 psi	500 psi	1000 psi	1500 psi
Thickness		0.064	0.062	0.061-0.062	0.064	0.057-0.060
Percent matrix		35.6	35.1	36.2	38.0	36.3
Peel lb/in	Top	7.0	6.4	7.0	6.9	10.0
	Bottom	7.1	6.8	7.5	7.3	6.7
Flex ksi	Long .	47.0	45.0	50.0	43.0	49.0
	Trans.	42.0	42.0	43.0	39.0	45.0

TABLE 6. SUMMARY OF LAMINATES PROPERTIES

Number	Foil	Fabric			Matrix		Thick- ness	Percent Matrix	Peel (lb/in)		Flex (Ksi)		Cond	CT/E
					Resin (Volume	Filler Percent)			Top	Bottom	Long.	Trans.		
26269-66	2G-2	7628	3HS-1	7628	AI-10	A-14	--	30	--	4.5	37	38	10.5	28.2
26269-68	2G-2	"	"	"	AI-10 (80)	A-14 (20)	0.066	37.8	--	2.7	38	--	12.5	21.4
26269-76	2 Ni	"	"	"	P13N	A-14	0.057	34.7	11.1	5.5	49	56	13.6	20
26269-83	2 Ni	"	"	"	P13N (80)	A-14 (20)	0.057	36.3	10.0	6.7	49	45	11.4	20
26269-84	2 Ni	--	H-31	--	P13N (80)	A-14 (20)	0.046	18.4	9.7	7.0	29	50	7.5	20
26269-85	2 Ni		H-31		"	"	0.050	24.9	9.6	7.4	24	25	8.4	17.5
26269-89	2 Ni	7628	201	7628	"	"	0.073	39.1	6.6	6.9	40	29	--	--
26269-90	2 Ni	"	H-31	"	"	"	0.065	45.0	5.6	5.6	39	29	--	--
26269-94	2 Ni	"	3HS-1	"	P13N (65)	A-14 (35)	0.061	45.4	7.6	7.8	41	37	14.8	20
27580-8	2 Ni	"	"	"	P13N (75)	A-14 (25)	0.056	37.1	6.8	7.0	42	47	9.56	11.8
27580-5	2 Ni	"	"	"	Special		0.056	43.9	8.0	7.8	41	33	--	24.9

TABLE 7. FLEX TESTS (ksi) AFTER 14 DAY CYCLE

Sample	Test	Start	7 Days	14 Days
26269-66 (AI-10)	Long.	37.0	36.9	33.7
	Trans.	38.0	32.0	36.9
27580-12 (P13N)	Long.	42.0	40.0	41.0
	Trans.	37.0	36.0	35.1
27580-15 (P13N)	Long.	42.0	41.0	43.6
	Trans.	37.0	35.0	38.3

TABLE 8. PEEL TESTS (lb/in) AFTER 14 DAY CYCLE

Sample	Test	Start	14 Days
26269-66 (AI-10)	Top	4.5	2.25
27580-12 (P13N)	Top	7.5	7.1
	Bottom	7.0	7.0
27580-15 (P13N)	Top	6.9	6.0
	Bottom	7.3	5.1



TABLE 9. WEIGHT LOSS OF P13N LAMINATE

Temperature	Weight	Percent Weight Loss	Percent Weight Loss/cm <sup>2</sup>
50 C	69.58 mg	0.17	0.41
100 C	69.47 mg	0.33	0.76
150 C	69.43 mg	0.39	0.90
200 C	69.42 mg	0.40	0.95
Isothermal at 200 C:			
<u>Hours</u>			
1	69.40 mg	0.43	1.02
2	69.40 mg	0.43	1.02
3	69.40 mg	0.43	1.02
4	69.40 mg	0.43	1.02
5	69.40 mg	0.43	1.02
6	69.40 mg	0.43	1.02
7	69.40 mg	0.43	1.02
8	69.40 mg	0.43	1.02
Overnight at 200 C:			
	69.40 mg	0.43	1.02

Area =  $(0.21 \text{ cm}^2) \times 2$ .

Starting weight = 69.70 mg.

TABLE 10. ESTIMATED PEEL STRENGTHS  
OF COPPER ADHESION

Laminate Identification (a)	Peel Strength, -- lb/in.	
	Side A	Side B
14 T	10.3	10.5
14 C	8.8	10.3
14 B	9.5	9.6
15 T	10.5	10.3
15 C	11.1	11.8
15 B	11.1	10.4

(a) Letter refers to position in stack, i.e., top, center, and bottom.

## APPENDIX B

### FIGURES

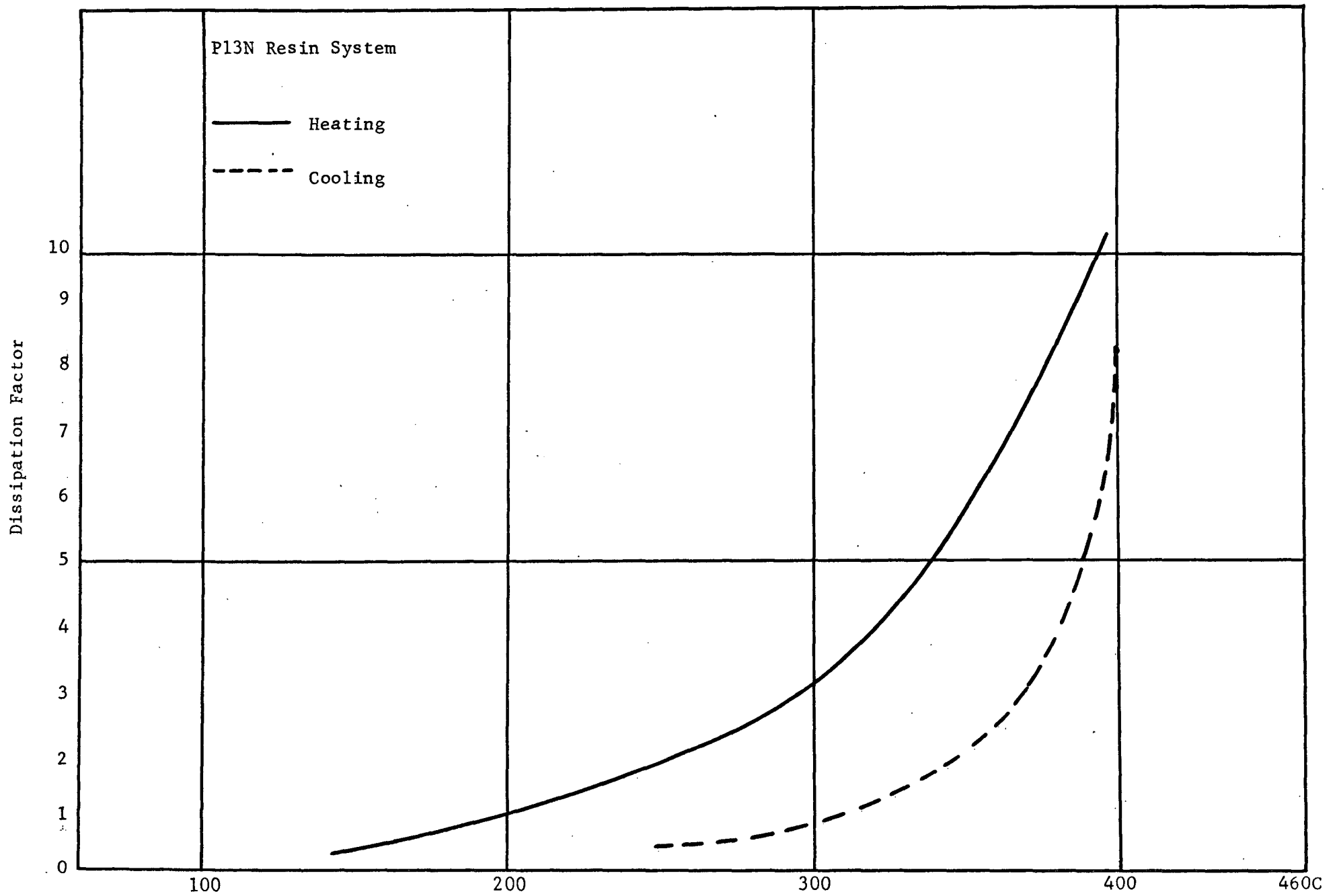


FIGURE 1. DISSIPATION FACTOR VS. LAMINATE TEMPERATURE (1 Cycle)

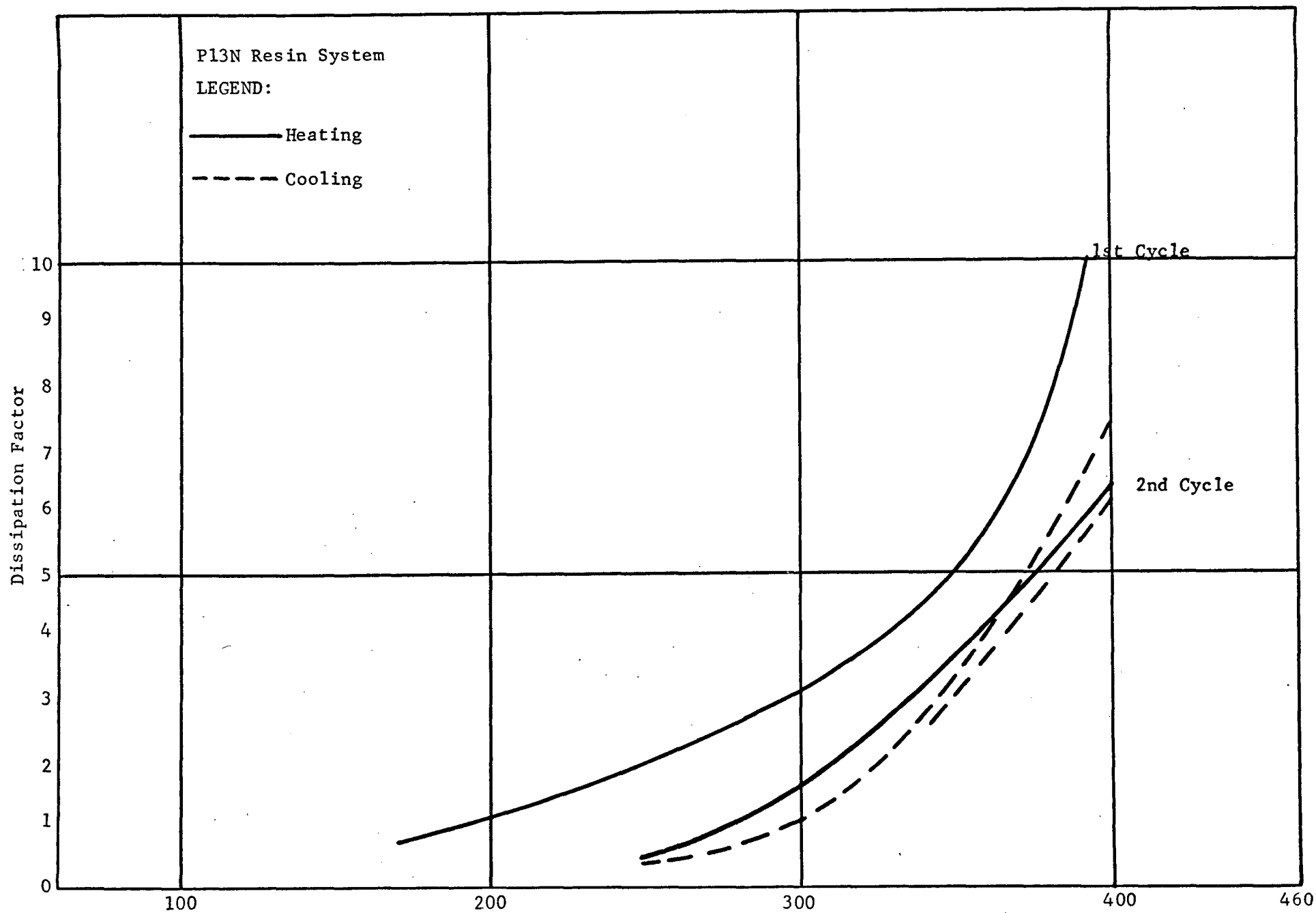


FIGURE 2. DISSIPATION FACTOR VS. LAMINATE TEMPERATURE (2 Cycles)

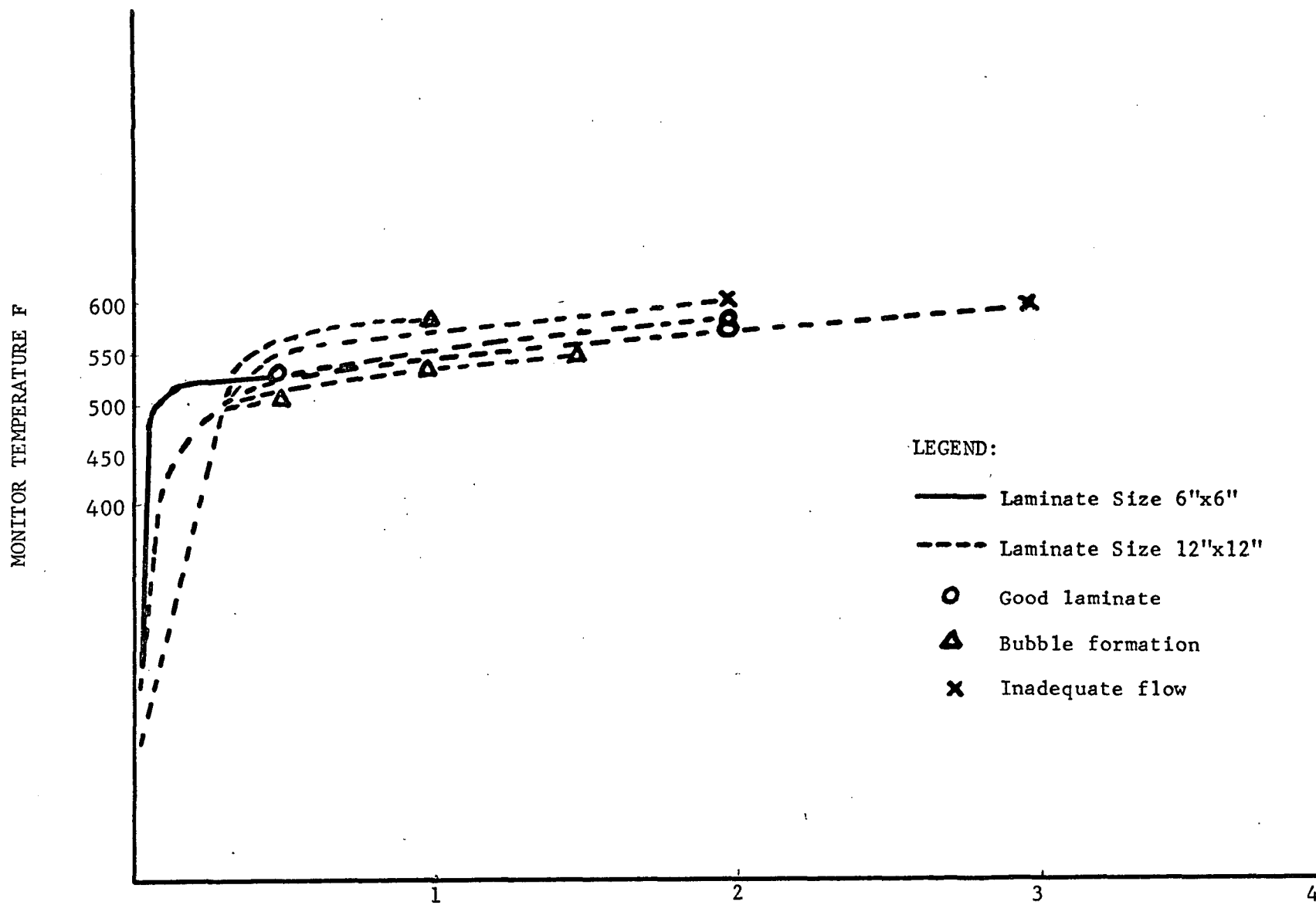
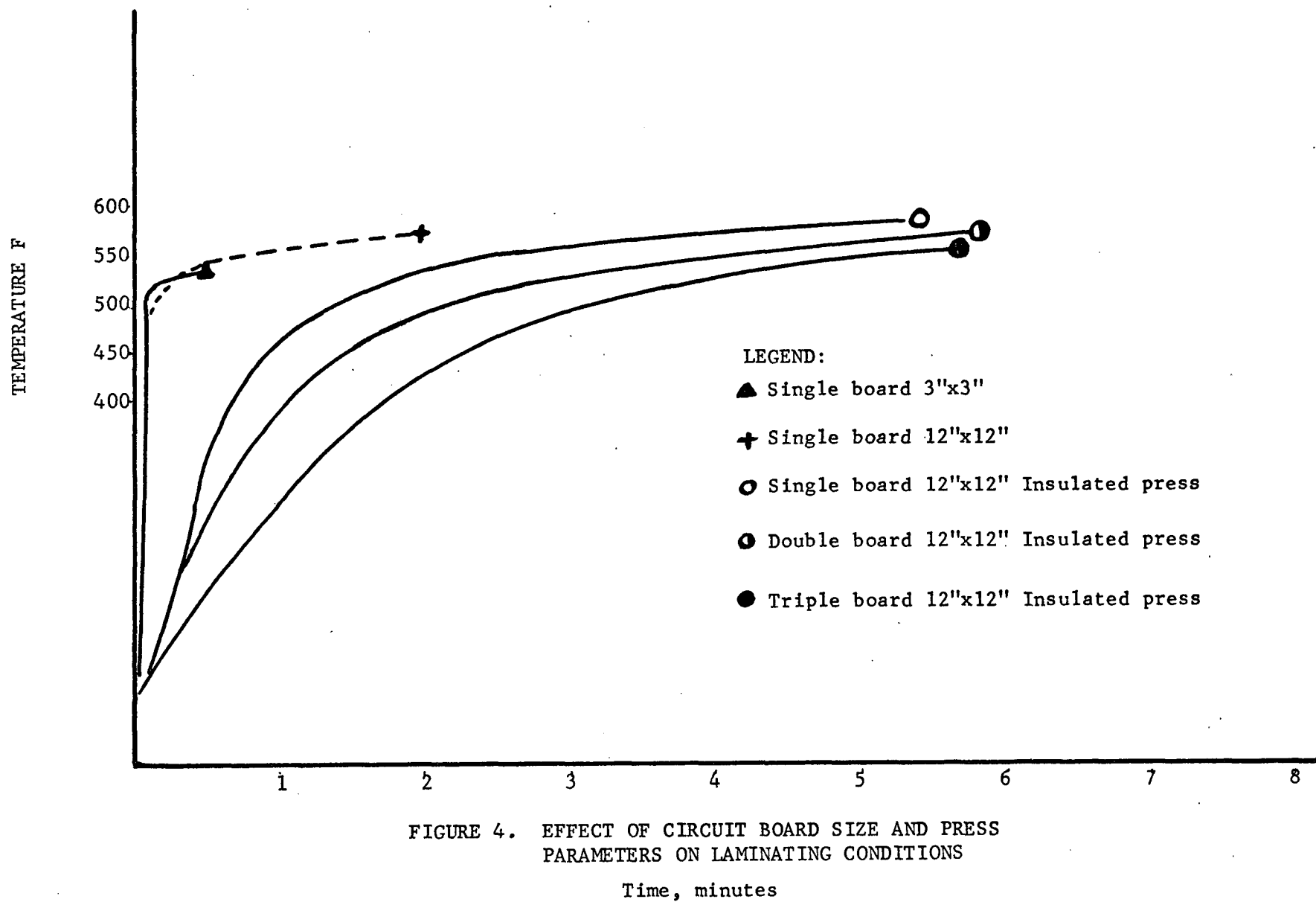
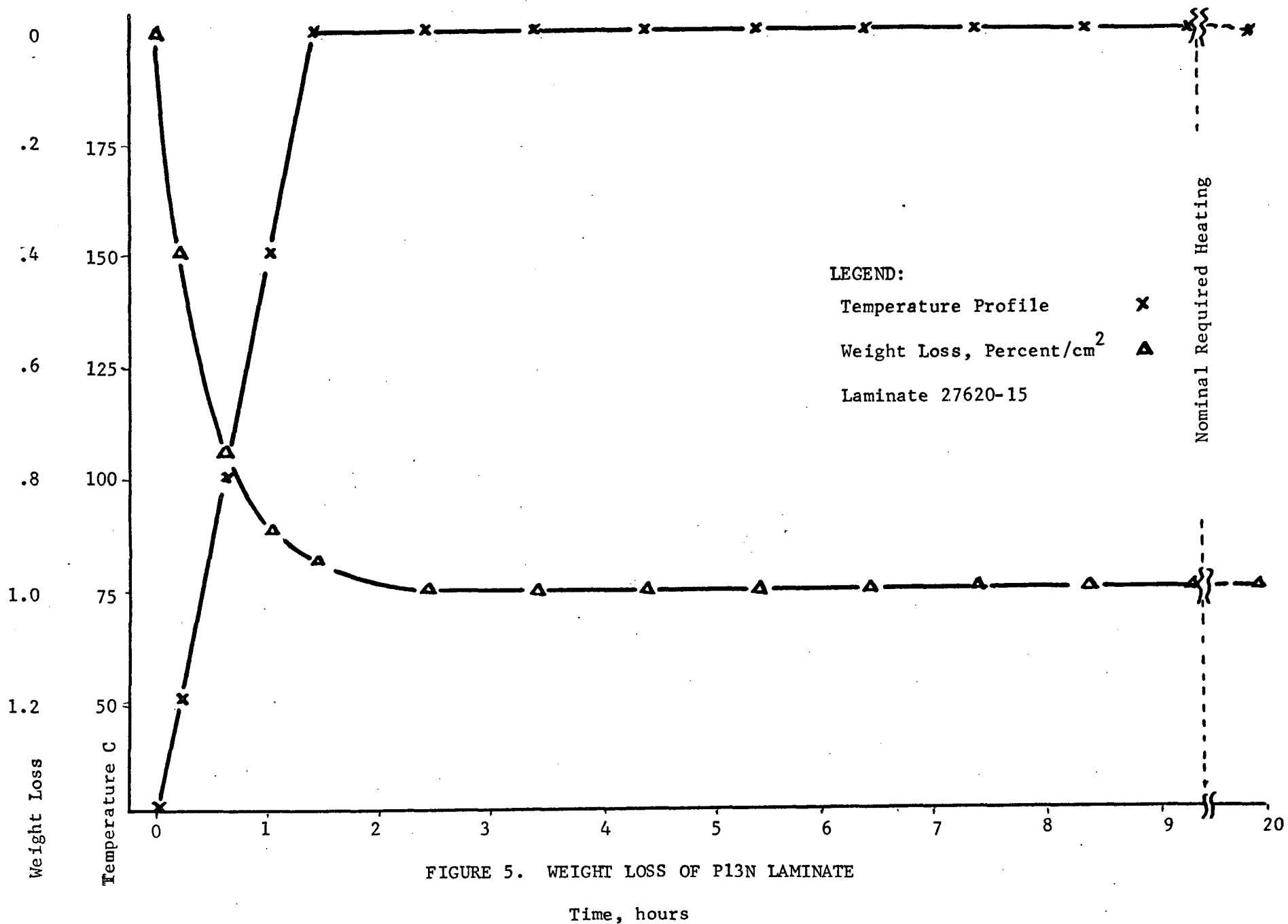


FIGURE 3. CORRELATION OF LAMINATE PROCESSING PARAMETERS







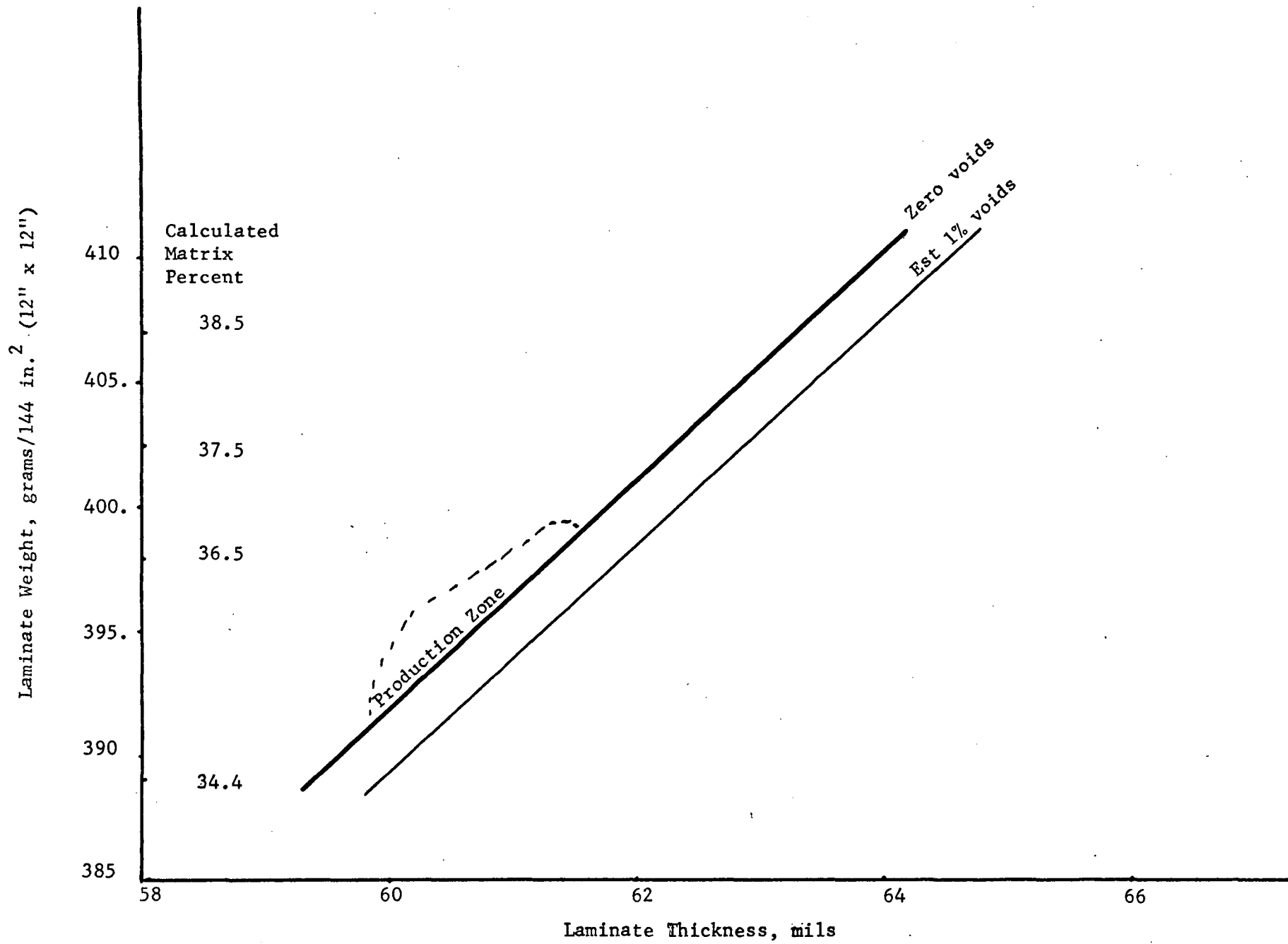
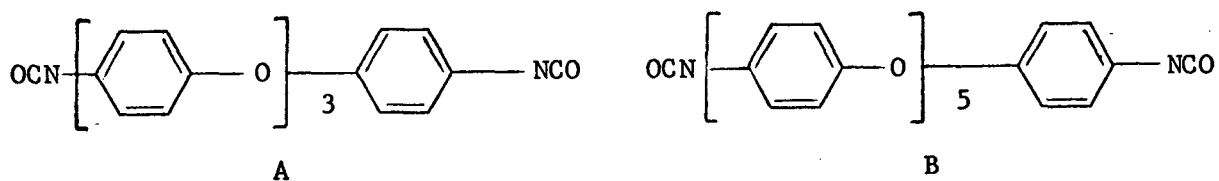


FIGURE 6. PROJECTION OF LAMINATE QUALITY

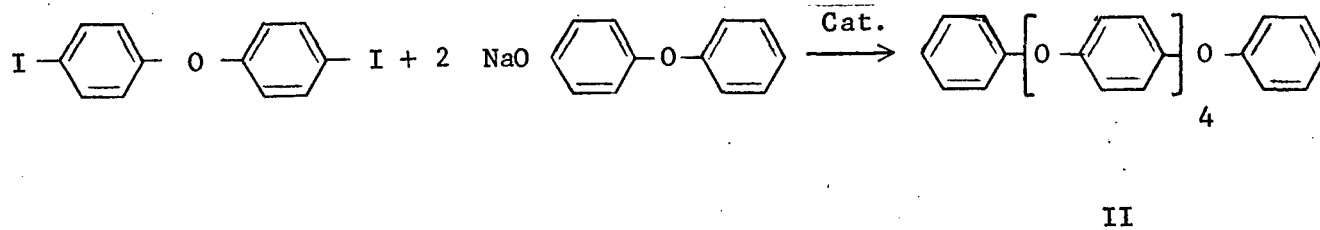
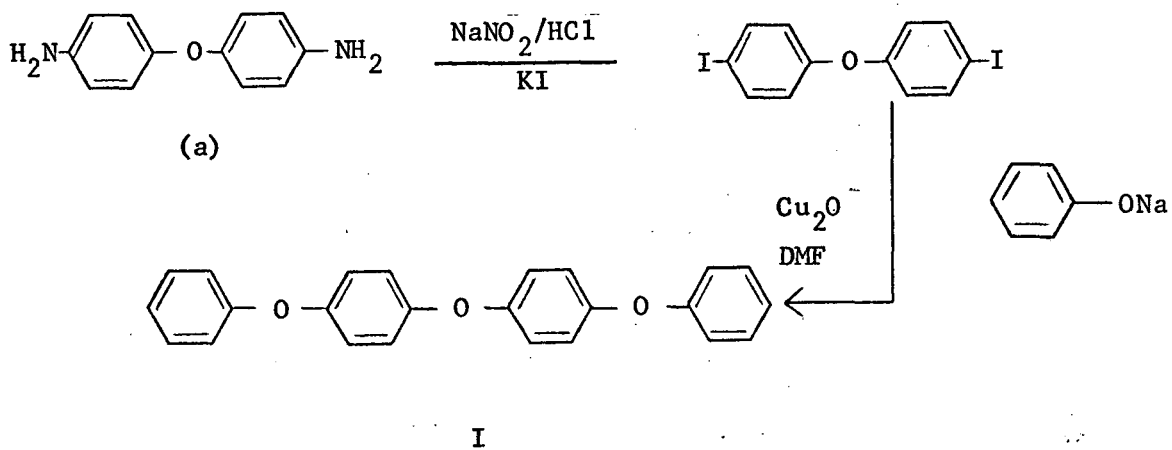
## APPENDIX C

### POLY(PHENYLENE OXIDE) DIISOCYANATE SYNTHESIS

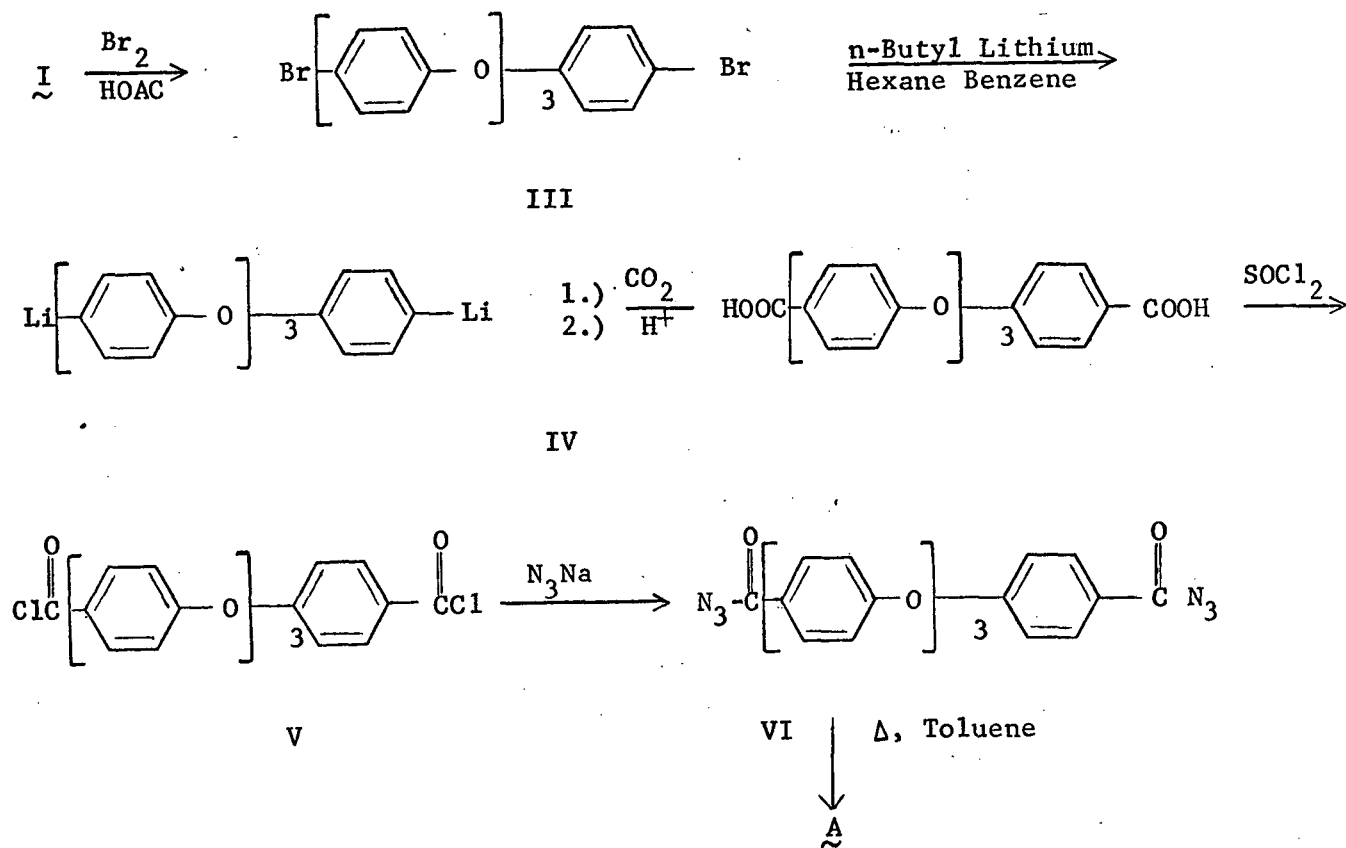
## APPENDIX C

POLY(PHENYLENE OXIDE) DIISOCYANATE SYNTHESIS

4,4'-bisphenoxydiphenylether (I) and 4,4'-bis-[4-phenoxyphenyl] diphenylether (II) were successfully prepared using the following reaction schemes.



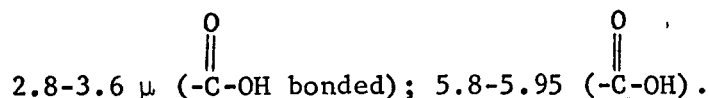
Diazotation of 4,4-diaminodiphenylether at -10°C with sodium nitrite/ aqueous HCl, followed by slow addition of the cold diazonium chloride to a boiling aqueous solution of potassium iodide gave, on aqueous bisulfite work-up, a 96 percent yield of crude 4,4'-diiododiphenylether. Two recrystallizations from acetone (cooling to -78°C) gave pure 4,4'-diiododiphenylether; melting point 138-139°C (literature melting point 138). Thin-layer chromatography on Silica Gel C showed the material to be homogeneous. Condensation of 4,4'-diiododiphenylether with a 40 percent excess of sodium phenoxide in refluxing DMF containing a half-mole equivalent of cuprous oxide (based on the diiododiphenylether) gave an 89 percent crude yield of I. One recrystallization from benzene methanol (1:4) yielded light tan crystals melting at 108-110°C (literature melting point 110°C). In like manner, condensation of 4,4'-diiododiphenylether with the sodium salt of 4-hydroxydiphenylether gave an 81.5 percent crude yield of II. One recrystallization from benzene gave II melting point 170-172°C (literature melting point 173°C). The p,p'-diisocyanate derivative of I was achieved by the following synthesis scheme.



The conversion of diphenylether (170 G) to 4,4'-dibromodiphenylether was accomplished with a 97 percent yield of product. Thin layer chromatographic analysis (tlc) of the product on Silica Gel G showed the material to be homogeneous. The dibromodiphenylether was then refluxed under argon in dry DMF with two moles of cuprous oxide and three moles of sodium phenoxide until tlc of the reaction mixture showed the absence of starting material (~ 120 hours). Quenching of the reaction in 10 percent aqueous sodium hydroxide precipitated tetramer I as a reddish purple solid rather than the expected light brown solid previously encountered in the smaller scale reactions. The solid was filtered and washed with six liters of 10 percent aqueous sodium hydroxide. The extensive washing with base succeeded in removing most of the reddish-purple color. The remaining dark gray-brown solid was vacuum dried then dissolved in hot benzene to give a dark reddish-brown solution. Several treatments of the solution with Norite failed to reduce its color. A rather large amount of solvent was necessary to prevent clogging the filter during filtration of the Norite-containing solution. The clogging problem was due to crystallization of the tetramer in the filter. The Norite treated benzene solution of the tetramer was then evaporated to dryness to give 265 g (75 percent) of partially purified I.

The partially purified tetramer (I) was brominated in hot glacial acetic acid to give, after precipitation in water- $\text{Na}_2\text{SO}_3$  and then drying, 411 g (80 percent) of crude brominated tetramer III. Again, purification of the product proved to be difficult. Only after four recrystallizations from benzene and four recrystallization from 1,2-dichloroethane was the pure dibromo tetramer (III) obtained (164.4 g; 40 percent) having a melting point of 171-172 C.

Treatment of III with n-butyl lithium in hexane/benzene followed by carboxylation with  $\text{CO}_2$  and acid work-up gave the desired acid IV in 92 percent yield. The infrared spectrum (KBr) of IV displayed the following bands:



IV was sparingly soluble in aqueous base.

The conversion of IV to the diacid chloride V was carried out by refluxing IV in  $\text{SOCl}_2$ . Distillation of  $\text{SOCl}_2$  followed by extraction of the residue with hot heptane afforded the diacid chloride V as a white solid in ~80 percent yield after evaporation of the heptane. The infrared spectrum of V shows the total disappearance of the  $2.8 \mu$  bonds for the acid hydroxyl groups and a shift of the acid carbonyl absorption from  $5.8 \mu - 5.95 \mu$  to  $5.65 \mu$  for the acid chloride.

Conversion of the diacid chloride (V) to the diazide VI was carried out in the following manner. The diacid chloride was dissolved in anhydrous acetone and the solution added rapidly to a cold, saturated solution of sodium azide in water. The reaction was stirred 10 minutes, filtered, and the white solid was vacuum dried for 24 hours over phosphorous pentoxide. The I.R. spectrum of the dried material displayed absorptions at  $6.0 \mu$

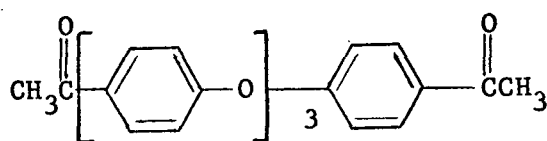
$\left( \begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{N}_3 \end{array} \right)$  and  $4.6 \mu \left( \begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{N}_3 \end{array} \right)$ . No absorption was observed at  $5.65 \mu$

$\left( \begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{Cl} \end{array} \right)$ .

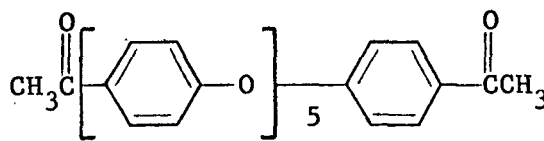
Pyrolysis of VI in hot toluene (80C) for six hours yielded the corresponding diisocyanate contaminated with the diazide. The I.R. (KBr) spectrum of the reaction residue displayed adsorption bonds for the presence of the starting diazide ( $6.0 \mu$  and  $4.6 \mu$ ) in addition to a new adsorption bond at  $4.4 \mu$  ( $-\text{NCO}$ ).

An alternative approach to the diisocyanate synthesis was discontinued when low yields were obtained in an oxidation step. Procedures and conditions involved in the alternative synthesis are summarized in the following discussion.

Compounds I and II were diacetylated using the following general procedure. The aromatic ether was dissolved or suspended in dichloromethane and added slowly to a solution of acetyl chloride-aluminum chloride in cold (0C) dichloromethane. After addition was complete, the reaction mixture was warmed to room temperature and stirred overnight (~12 hours). The mixture was then poured over crushed ice and extracted with dichloromethane. The extracts were combined and washed with water until the washings were neutral to hydriion paper. The solution was then dried over calcium chloride, filtered and the solvent evaporated to give the desired diacetylated compound. The crude yields of VI and VII obtained were 96 percent and 94 percent, respectively. Infrared spectra of both VI and VII contain a strong

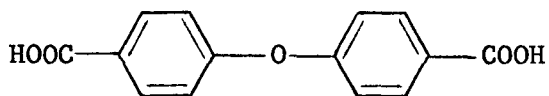


VI



VII

absorption at  $6.0 \mu$  ( $\text{CH}_3\text{C}=\text{O}$ ). In addition, both spectra lack the mono-substitution bands of the starting materials at  $\sim 13.5 \mu$  and  $14.5 \mu$ . An attempted oxidation of VI to the corresponding diacid with aqueous sodium hypochlorite gave an acidic material whose I.R. was similar to that of the diacid of diphenylether (VIII). The yield of this oxidation product was low



VIII

(~20%) with the remaining material (as shown by I.R.) composed mainly of starting diketone (VI). An oxidation of VI with I<sub>2</sub> in pyridine, followed by base hydrolysis was also unsuccessful. The I.R. spectrum of IY was superimposable on that of the acidic material obtained from the hypochlorite oxidation of VI. It is interesting to note that IY was sparingly soluble in aqueous base. This behavior explains in part why the hypochlorite oxidation failed to give good yields of the diacid in that as the oxidation of the diacetyl compound progresses it becomes coated with the insoluble acid salt which inhibits further oxidation. It was at this step that this route to synthesis was discontinued and work started on the successful procedure discussed initially.

## APPENDIX D

### CIRCUIT BOARD PRODUCTION



## APPENDIX D

CIRCUIT BOARD PRODUCTION  
(Materials and Procedures)

## I. Materials and Sources

- A. P13N Polyimide Resin  
TRW Systems, Redondo Beach, California  
Geigy Chemical, Ardsley, New York
- B. GT treated Copper Foil  
Circuit Foil Corporation, Bordentown, New Jersey
- C. 7628 Fabric  
Burlington Glass Fabrics, New York, New York
- D. Tricon HS-1 Fabric  
A. Wimpfheimer & Brothers, Inc., Stonington, Connecticut
- E. Alumina (A-14) Hard Fired, Ball Milled  
Alcoa
- F. A-1100 Coupling Agent  
Union Carbide Silicones Division  
New York, New York

## II. Impregnating Systems

- A. Resin TRW P13N Polyimide  
Solids, percent  $40 \pm 2.0$   
Solvent Dimethyl Formamide  
Viscosity at 25 C - 200-300 cps
- B. Copper Primer  
Resin (A) - 2 mil dried coating
- C. Fabric Impregnating System
 

Resin 40 percent solid	- 75.20 w/o (weight percent)
Alumina (A-14)	24.03 w/o
A-1100	.77 w/o

Any mixing procedure with sufficient shear to break up powder agglomerates can be used. Experimental systems have been homogenized by rolling a can containing ceramic balls on slow-speed rolls. Larger quantities have been blended using a dispersator high-speed mixer, however, care must be taken to avoid heating the system.

### III. Coating and Impregnating Procedures

A Dixon coater was used for coating both the 7628 and HS-1 fabric. The coating traverse and conditions used are shown in Figure D-1. Good wetting and pickup was obtained with this system. Nip-roll settings of 15 and 31 mils were used for the 7628 and HS-1 reinforcements respectively. Maximum dwell time (15 minutes) was adequate to dry the system to touch, but not to a tack-free state. Consequently, a thin Mylar parting film was fed into the roll in the rewind step. Some tacking to the Teflon-coated rolls was experienced due to the slow drying characteristics of the solvent. Accordingly, it is believed that a 30 foot or higher vertical oven would perform somewhat better with this system. Although recommended drying time for the P13N resin is 15 minutes at 150 F, experience has shown that blistering occurs unless a longer drying time is used. In the absence of a continuous unit for completion of the drying and prepregging step, these reinforcements were sectioned into sheets 12-1/2 x 12-1/2 inches for subsequent laminating. A number of sheets were suspended on a light-weight metal frame and placed first in a 150 F oven for 30 minutes followed by 1 hour in a 400 F oven.

Laminating sized sheets of copper (12-3/4 x 12-3/4 inches) were slipped to light-weight metal plates, coated, and placed first in a 150 F oven for 1/2 hour followed by 1 hour in a 400 F oven. No difficulty was noted in the processing or handling of either the impregnated fabrics or the coated foil which would preclude the use of continuous units with the necessary range of speeds and temperatures.

### IV. Laminating Procedures

- A. Sheet preparation--None was needed. However, these may be pre-flattened, if necessary, by lightly pressing in a 150 C press. (Conventional impregnation and drying procedures provide adequate constraint that this precaution is unnecessary.) Sheets are trimmed to a square pattern.
- B. Lay-up--This consists of a three-ply HS-1 core and a single ply of 7628 cloth on each side. Each ply is rotated 90° from the previous ply in the stack. The lay-up is topped with the precoated copper foil.
- C. Stabilization--Small sized laboratory lay-ups including the 12-1/2 x 12-1/2-inch laminates were tied to prevent shifting. Larger sized lay-ups should have adequate contact area to prevent significant shift during pressing.
- D. Isolation plates--1/32 inch polished stainless steel sheets.

- E. Preheat and volatile reduction--Contact pressure in a preheated (650 F) press for time necessary to degas and heat matrix. Time is highly dependent upon heating rate, and rapid heating appears desirable. Press controls reduced to 600 F before insertion of laminate. (Contact time may be as short as 30 seconds or as long as 6-1/2 minutes depending upon heating rate.)
- F. Lamination--Raise pressure to 1000 to 1500 psi and hold 1 hour at 600 F.
- G. Board may be cooled under pressure or pulled hot. It is advisable, however, to keep the stack intact to minimize thermal shock and possible warping.

#### V. Specifications

- A. Matrix: Development studies indicate a good balance of thermal properties are achieved at a filler level of 22.5 volume-percent. This is the basis of formulation II-C.
- B. Prepreg: Laminate fabrication and properties appear to reach an optimum around 35 w/o matrix in the fabrics. Accordingly, impregnation is targeted to this value.
- C. Copper primer: Two mils of P13N after drying and prepreging is desired.
- D. Laminate: When fabricated with the following components:

Copper	Two faces - 2 mils neat resin
7628	Two plies - 35 w/o matrix
HS-1	Three plies - 35 w/o matrix

and laminated to a good quality CB, the thickness falls within the thickness tolerances of the G-10 specifications. Physical and electrical properties are comparable to G-10 specification. Flexural strengths of the P13N CB system are about 1000 psi lower than G-10 specifications. Thermal properties, conductivity and expansion, of this CB are much improved over the G-10 system.

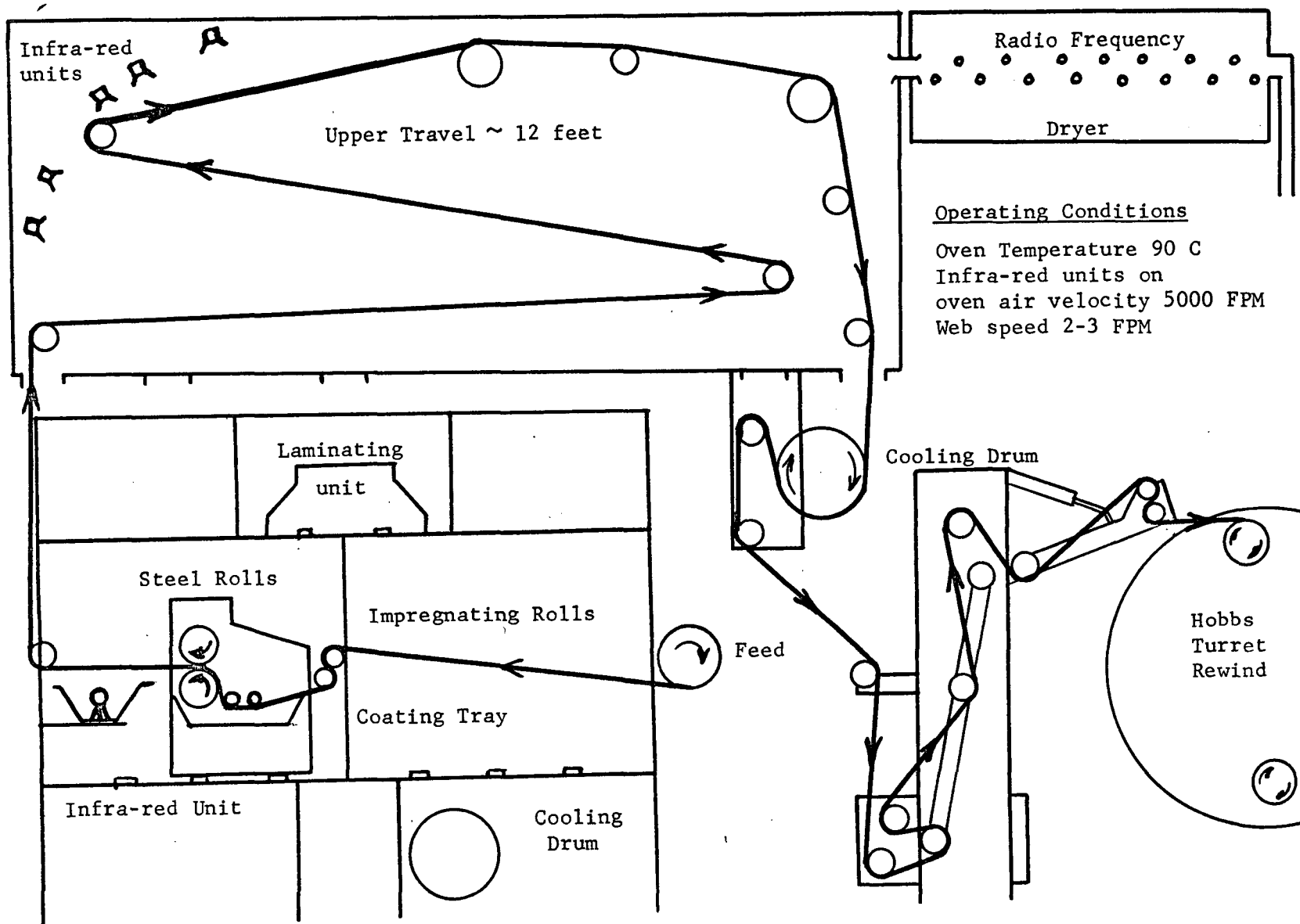


FIGURE D-1. DIXON COATER